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An experimental test of the Jarzynski equality in a mechanical experiment

F. Douarche, S. Ciliberto, A. Petrosyan I. Rabbiosi
Laboratoire de Physique de l'ENS Lyon CNRS UMR 5672
46, Allée d'Italie - 69364 Lyon Cedex 07, France

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Abstract

We have experimentally checked the Jarzynski equality and the Crooks relation [1, 2, 3] on the thermal fluctuations of a macroscopic mechanical oscillator in contact with a heat reservoir. We found that, independently of the time scale and amplitude of the driving force, both relations are satisfied. These results give credit, at least in the case of Gaussian fluctuations, to the use of these relations in biological and chemical systems to estimate the free energy difference ΔF between two equilibrium states [4, 5]. An alternative method to estimate ΔF in isothermal process is proposed too.

1 Introduction

Many systems in Nature and in technological applications work out of equilibrium. However, a precise estimation of the free energy difference ΔF between two equilibrium states A and B of these systems is extremely useful to increase our knowledge of the underlying physical processes which control their dynamical behaviour. It is well known that ΔF can be estimated by perturbing the system with an external parameter λ and by measuring the work W done to drive the system from A to B . However this method gives in general an overestimation of ΔF because $W \geq \Delta F$, where the equality holds if and only if the perturbation is infinitely slow. In other words the path γ to go from A to B has to be a reversible one. In many systems, because of unavoidable experimental and environmental constraints, the path γ is not a reversible one, that is the system cannot be driven from A to B in a time much longer than its relaxation time. This may happen for example in all the systems where thermal fluctuations cannot be neglected and the external power injected into the system is comparable to the thermal energy. In 1997 [1] Jarzynski derived an equality which relates the free energy difference of a system in contact with a heat reservoir to the probability distribution function (pdf) of the work performed on the system to drive it from A to B along any path γ in the system parameter space. Specifically, when λ is varied from time $t = 0$ to $t = t_s$, Jarzynski defines for one realization of the “switching process” from A to B the work performed on the system as

$$W = \int_0^{t_s} \dot{\lambda} \frac{\partial H_\lambda[z(t)]}{\partial \lambda} dt, \quad (1)$$

where z denotes the phase-space point of the system and H_λ its λ -parametrized Hamiltonian (see also [6]). One can consider an ensemble of realizations of this “switching process” with initial conditions all starting in the same initial equilibrium state. Then W may be computed for each trajectory in the ensemble. The Jarzynski equality (JR) states that [1]

$$\Delta F = -\frac{1}{\beta} \log \langle \exp [-\beta W] \rangle, \quad (2)$$

where $\langle \cdot \rangle$ denotes the ensemble average, $\beta^{-1} = k_B T$ with k_B the Boltzmann constant and T the temperature. In other words $\langle \exp [-\beta W_{\text{diss}}] \rangle = 1$, since we can always write $W = \Delta F + W_{\text{diss}}$ where W_{diss} is the dissipated work. Thus it is easy to see that there must exist some paths γ such that $W_{\text{diss}} \leq 0$. Moreover, the inequality $\langle \exp x \rangle \geq \exp \langle x \rangle$ allows us to recover the second principle, namely $\langle W_{\text{diss}} \rangle \geq 0$, i.e. $\langle W \rangle \geq \Delta F$. From an experimental point of view the JE is quite useful because there is no restriction on the choice of the path γ and it overcomes the above mentioned experimental difficulties. Numerous derivations of the JE has been produced [7, 8, 9, 10, 11], but it seems from the recent criticisms of Cohen and Mauzerall [12] that this result is still under debate. Without willing to enter in this letter into the theoretical debate, we think that it is important to experimentally check the JE on a very simple and controlled system in order to safely use it in more complex cases as the biological and chemical ones, where it is much more difficult to verify the results with other methods. For this reason we experimentally probe a model system: a macroscopic mechanical oscillator driven out of equilibrium, between two equilibrium states A and B , by a small external force. We show that the JE is experimentally accessible and valid, and does not depend on the oscillator’s damping, on the driving force’s switching rate and on its amplitude. In our experiment we can also check the Crooks relation (CR) which is somehow related to the JE and which gives useful and complementary information on the dissipated work. Crooks considers the forward work W_f to drive the system from A to B and the backward work W_b to drive it from B to A . If the work pdfs during the forward and backward processes are $P_f(W)$ and $P_b(W)$, one has [2, 3]

$$\frac{P_f(W)}{P_b(-W)} = \exp (\beta[W - \Delta F]) = \exp [\beta W_{\text{diss}}]. \quad (3)$$

A simple calculation from Eq. (3) leads to Eq. (2). However, from an experimental point of view this relation is extremely useful because one immediately sees that the crossing point of the two pdfs, that is the point where $P_f(W) = P_b(-W)$, is precisely ΔF . Thus one has another mean to check the computed free energy by looking at the pdfs crossing point ΔF_\times . Let us examine in some detail the Gaussian case: $P(W) \propto \exp \left(-\frac{[W - \langle W \rangle]^2}{2\sigma_W^2} \right)$ leads to $\Delta F = \langle W \rangle - \frac{\beta\sigma_W^2}{2}$, i.e. $\langle W_{\text{diss}} \rangle = \frac{\beta\sigma_W^2}{2} > 0$. Furthermore, it is easy to see from Eq. (3) that if $P_f(W)$ and $P_b(-W)$ are Gaussian, then $\Delta F = \frac{\langle W \rangle_f - \langle W \rangle_b}{2}$ and $\beta\sigma_W^2 = \langle W \rangle_f + \langle W \rangle_b = 2 \langle W_{\text{diss}} \rangle$. Thus in the case of Gaussian statistics ΔF and $\langle W_{\text{diss}} \rangle$ can be computed by using just the mean values and the variance of the work W .

Before describing the experiment, we want to discuss several important points. The first is the definition of the work given in Eq. (1), which is not the classical one. Let us consider, for example, that λ is a mechanical torque M applied to a mechanical system Ξ , and $-\partial H_\lambda / \partial \lambda$ the associated angular displacement θ . Then, from Eq. (1), one has

$$W = - \int_0^{t_s} \dot{M} \theta dt = - [M \theta]_0^{t_s} - W^{\text{cl}} \quad \text{where} \quad W^{\text{cl}} = - \int_0^{t_s} M \dot{\theta} dt \quad (4)$$

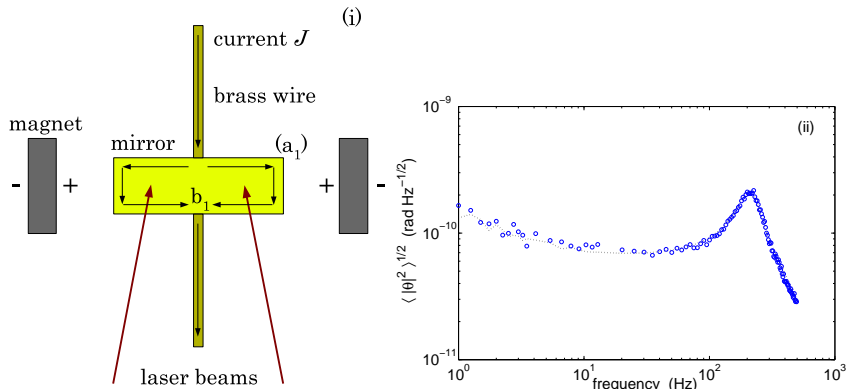


Figure 1: (i) Schematic drawing of the oscillator; (ii) FDT check in oil: the circles (\circ) correspond to the direct measurement of the noise and the dashed curve is $\sqrt{\langle |\hat{\theta}|^2 \rangle}$ computed by inserting the measured response function in the FDT, Eq. (7)

is the classical work. Thus W and W^{cl} are related but they are not exactly the same and we will show that this makes an important difference in the fluctuations of these two quantities. The second point concerns the ΔF computed by the JE in the case of a driven system, composed by Ξ plus the external driving. The total free energy difference is $\Delta F = \Delta F_0 - \Phi$ where ΔF_0 is the free energy of Ξ and $\Phi = \left[M\theta \right]_A^B$ the energy difference of the forcing. The JE computes the ΔF of the driven system and not that of the system alone which is ΔF_0 . This is an important observation in view of all applications where an external parameter is added to Ξ in order to measure ΔF_0 [5]. Finally we point out that, in an isothermal process, ΔF_0 can be easily computed, without using the JE and the CR, if W^{cl} is Gaussian distributed with variance $\sigma_{W^{\text{cl}}}^2$. Indeed the crossing point W_{\times}^{cl} of the two Gaussian pdfs $P_f(W^{\text{cl}})$ and $P_b(-W^{\text{cl}})$ is

$$W_{\times}^{\text{cl}} = \frac{\langle W^{\text{cl}} \rangle_f - \langle W^{\text{cl}} \rangle_b}{2}, \quad (5)$$

which by definition is just $-\Delta F_0$, i.e. $W_{\times}^{\text{cl}} = -\Delta F_0$. Furthermore $\langle W^{\text{cl}} \rangle_f + \langle W^{\text{cl}} \rangle_b = -2 \langle W_{\text{diss}} \rangle$ by definition, but in this case $2 \langle W_{\text{diss}} \rangle \neq \beta \sigma_{W^{\text{cl}}}^2$.

2 Experimental setup

To study the JE and the CR we measure the out-of-equilibrium fluctuations of a macroscopic mechanical torsion pendulum made of a brass wire, whose damping is given either by the viscoelasticity of the torsion wire or by the viscosity of a surrounding fluid. This system is enclosed in a cell which can be filled with a viscous fluid, which acts as a heat bath. A brass wire of length 10 mm, width 0.75 mm, thickness $50 \mu\text{m}$, mass $5.91 \times 10^{-3} \text{ g}$, is clamped at both ends, hence its elastic torsional stiffness is $C = 7.50 \times 10^{-4} \text{ N m rad}^{-1}$. A small mirror of effective mass $4.02 \times 10^{-2} \text{ g}$, length 2.25 mm, width $b_1 = 7 \text{ mm}$, thickness $a_1 = 1.04 \text{ mm}$, is glued in the middle

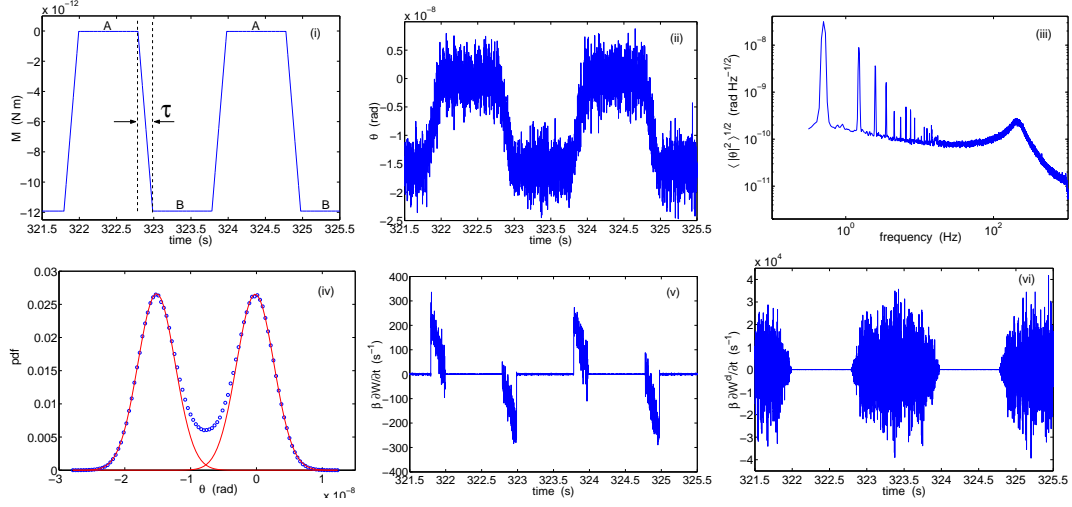


Figure 2: Oscillator immersed in oil [case (a)]: (i) Applied external torque, (ii) Induced angular displacement, (iii) its psd, (iv) its pdf, (v) Injected power computed from the Jarzynski definition $\dot{W} = -\dot{M}\theta$, (vi) Injected power computed from the standard definition $\dot{W}^{\text{cl}} = -M\dot{\theta}$

of the wire, see Fig. 1(i), so that the moment of inertia of the wire plus the mirror in vacuum is $I = 1.79 \times 10^{-10} \text{ kg m}^2$ (whose main contribution comes from the mirror). Thus the resonant frequency of the pendulum in vacuum is $f_0 = 326.25 \text{ Hz}$. When the cell is filled with a viscous fluid, the total moment of inertia is $I_{\text{eff}} = I + I_{\text{fluid}}$, where I_{fluid} is the extra moment of inertia given by the fluid displaced by the mirror [13]. Specifically, for the oil used in the experiment (which is a mineral oil of optical indice $n = 1.65$, viscosity $\nu = 121.3 \text{ mPa s}$ and density $\rho = 0.9 \rho_{\text{water}}$ at $T = 21.3^\circ \text{C}$) the resonant frequency becomes $f_0 = 213 \text{ Hz}$. To apply an external torque M to the torsion pendulum, a small electric coil connected to the brass wire is glued in the back of the mirror. Two fixed magnets on the cell facing each other with opposite poles generate a static magnetic field. We apply a torque by varying a very small current J flowing through the electric coil, hence $M \propto J$. The measurement of the angular displacement of the mirror θ is done using a Nomarski interferometer [14, 15] whose noise is about $6.25 \times 10^{-12} \text{ rad}/\sqrt{\text{Hz}}$, which is two orders of magnitude smaller than the oscillator thermal fluctuations. A window on the cell allows the laser beams to go inside and outside. Much care has been taken in order to isolate the apparatus from the external mechanical and acoustic noise, see [16] for details.

The motion of the torsion pendulum can be assimilated to that of a harmonic oscillator damped by the viscoelasticity of the torsion wire and the viscosity of the surrounding fluid, whose motion equation reads in the temporal domain

$$I_{\text{eff}} \ddot{\theta} + \int_{-\infty}^t G(t-t') \dot{\theta}(t') dt' + C\theta = M, \quad (6)$$

where G is the memory kernel. In Fourier space (in the frequency range of our interest) this equation takes the simple form $[-I_{\text{eff}} \omega^2 + \hat{C}] \hat{\theta} = \hat{M}$, where $\hat{\cdot}$ denotes the Fourier transform and

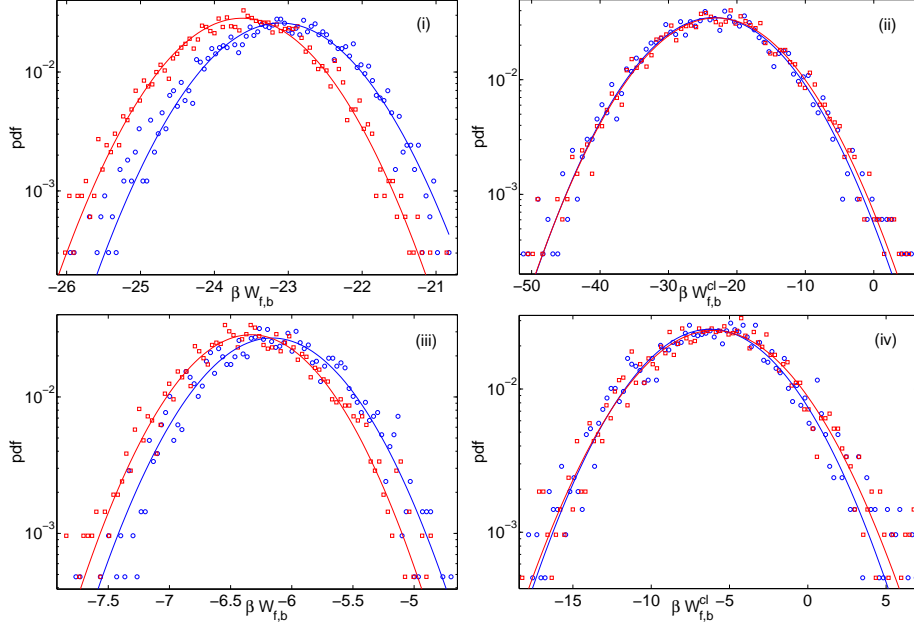


Figure 3: Case a): (i) $P_f(W)$ and $P_b(-W)$, (ii) $P_f(W^{cl})$ and $P_f(-W^{cl})$; Case c): (iii) $P_f(W)$ and $P_b(-W)$, (iv) $P_f(W^{cl})$ and $P_f(-W^{cl})$ (experimental forward and backward pdfs are represented by \circ and \square respectively, whereas the continuous lines are Gaussian fits)

$\hat{C} = C + i[C_1'' + \omega C_2'']$ is the complex frequency-dependent elastic stiffness of the system. C_1'' and C_2'' are the viscoelastic and viscous components of the damping term. The response function of the system $\hat{\chi} = \hat{\theta}/\hat{M}$ can be measured by applying a torque with a white spectrum. When $M = 0$, the amplitude of the thermal vibrations of the oscillator is related to its response function via the fluctuation-dissipation theorem (FDT) [6]. Therefore, the thermal fluctuation power spectral density (psd) of the torsion pendulum reads for positive frequencies

$$\langle |\hat{\theta}|^2 \rangle = \frac{4k_B T}{\omega} \text{Im} \hat{\chi} = \frac{4k_B T}{\omega} \frac{C_1'' + \omega C_2''}{[-I_{\text{eff}} \omega^2 + C]^2 + [C_1'' + \omega C_2'']^2}. \quad (7)$$

We plot in Fig. 1(ii) the measured thermal square root psd of the oscillator. The measured noise spectrum [circles in Fig. 1(ii)] is compared with the one estimated [dotted line in Fig. 1(ii)] by inserting the measured $\hat{\chi}$ in the FDT, Eq. (7). The two measurements are in perfect agreement and obviously the FDT is fully satisfied because the system is at equilibrium in the state A where $M = 0$ (see below). Although this result is expected, this test is very useful to show that the experimental apparatus can measure with a good accuracy and resolution the thermal noise of the macroscopic pendulum.

3 Experimental results

Now we drive the oscillator out of equilibrium between two states A (where $M = 0$) and B (where $M = M_{\max} = \text{const} \neq 0$). The path γ may be changed by modifying the time evolution of M between A and B . We have chosen either linear ramps with different rising times τ , see Fig. 2(i), or half-sinusoids with half-period τ . In the specific case of our harmonic oscillator, as the temperature is the same in states A and B , the free energy difference of the oscillator alone is $\Delta F_0 = \Delta U = \left[\frac{1}{2} C \theta^2 \right]_A^B = \left[\frac{M^2}{2C} \right]_A^B$, whereas $\Delta F = \Delta F_0 - \left[\frac{M^2}{C} \right]_A^B$, i.e. for an harmonic potential $\Delta F = -\Delta F_0$. Let us first consider the situation where the cell is filled with oil. The oscillator's relaxation time is $\tau_{\text{relax}} = 23.5$ ms. We apply a torque which is a sequence of linear increasing/decreasing ramps and plateaux, as represented in Fig. 2(i). We chose different values of the amplitude of the torque M [11.9, 6.1, 4.2 and 1.2 pN m] and of the rising time τ [199.5, 20.2, 65.6, 99.6 ms, respectively], as indicated in Table 1 [cases a)...e)]. Thus we can probe either the reversible (or quasi-static) paths ($\tau \gg \tau_{\text{relax}}$) or the irreversible ones ($\tau \lesssim \tau_{\text{relax}}$). We tune the duration of the plateaux (which is at least $4\tau_{\text{relax}}$) so that the system always reaches equilibrium in the middle of each of them, which defines the equilibrium states A and B . We see in Fig. 2(ii), where the angular displacement θ is plotted as a function of time [case a)], that the response of the oscillator to the applied torque is comparable to the thermal noise spectrum. The psd of θ is shown in Fig. 2(iii). Comparing this measure with the FDT prediction obtained in Fig. 1(ii), one observes that the driver does not affect the thermal noise spectrum which remains equal to the equilibrium one. Moreover we plot in Fig. 2(iv) the pdf of the driven displacement θ shown on Fig. 2(ii), which is, roughly speaking, the superposition of two Gaussian pdfs. From the measure of M and θ , the power injected into the system \dot{W} can be computed from the definition given in Eq. (1), that in this case is $\dot{W} = -\dot{M}\theta$. Its time evolution, shown in Fig. 2(v), is quite different from that of the classical power $\dot{W}^{\text{cl}} = -M\dot{\theta}$, whose time evolution is plotted on Fig. 2(vi): \dot{W} is non-zero only for $\dot{M} \neq 0$ and vice-versa $\dot{W}^{\text{cl}} \neq 0$ only for $M \neq 0$. From one time series of \dot{W} we can compute from Eq. (1) the forward and the backward works, W_f and W_b , corresponding to the paths $A \rightarrow B$ and $B \rightarrow A$, respectively. We also do the same for the classical work. We then compute their respective pdfs $P_f(W)$ and $P_b(-W)$. These are plotted on Figs. 3(i,iv) where the bullets are the experimental data and the continuous lines their fitted Gaussian pdfs. In Figs. 3, the pdfs of W and W^{cl} cross in the case a) at $\beta W \simeq -23.5$, and in the case c) $\beta W \simeq -6.1$. These values correspond to the $\Delta F = -\frac{M_{\max}^2}{2C} = -\Delta F_0$. We find that this result is true independently of the ratio τ/τ_{relax} and of the maximum amplitude of $|M|$, M_{\max} . This can be seen on Table 1, where the computed $\Delta U = \frac{M_{\max}^2}{2C}$ is in good agreement with the values obtained by the crossing points of the forward and backward pdfs, that is $\Delta F_{\times} + \Phi$ for $P(W)$ and $-\Delta W_{\times}^{\text{cl}}$ for $P(W^{\text{cl}})$. Finally inserting the values of W_f and W_b in Eq. (2) we directly compute ΔF_f and ΔF_b from the JE. As can be seen in Table 1, the values of ΔF_0 obtained from the JE, that is either $-(\Delta F_f + \Phi)$ or $-(\Delta F_b + \Phi)$, agree within experimental errors with the computed ΔU . Indeed JE works well either in the foreseeable case a) where $\tau \gg \tau_{\text{relax}}$ or in the critical case b) where $\tau \lesssim \tau_{\text{relax}}$. The other case we have studied is a very pathological one. Specifically, the oscillator is in vacuum and has a resonant frequency $f_0 = 353$ Hz and a relaxation time $\tau_{\text{relax}} = 666.7$ ms. We applied a sinusoidal torque whose amplitude is either 5.9×10^{-12} or 9.4×10^{-12} N m [cases f) and g) in Table 1, respectively]. Half a period of the sinusoid is $\tau = 49.5$ ms, much smaller than the relaxation time, so that we never let the system equilibrate. However, we define the states A and B as the maxima and minima of the driver. Surprisingly, despite of the pathological definition of the equilibrium states A and

τ/τ_{relax}	M_{max}	$-\beta[\Delta F_{\text{f}} + \Phi]$	$\beta[\Delta F_{\text{b}} + \Phi]$	$-\beta[\Delta F_{\times} + \Phi]$	$-\beta W_{\times}^{\text{cl}}$	$\beta\Delta U$	$ \beta\Delta F_{\odot} $
8.5 ^{a)}	11.9	23.5	23.1	23.5	23.4	23.8	1.0
0.85 ^{b)}	6.1	5.9	5.4	6.0	7.0	6.0	1.0
3.5 ^{c)}	6.1	6.1	5.9	6.5	6.1	6.1	0.4
2.8 ^{d)}	4.2	2.8	2.6	3.2	2.9	2.7	0.3
4.2 ^{e)}	1.2	0.21	0.20	0.22	0.21	0.22	0.04
0.07 ^{f)}	5.9	10.3	10.0	10.1	10.1	10.3	0.4
0.07 ^{g)}	9.4	67.4	65.5	66.8	66.4	67.5	2.4

Table 1: Free energies of cases a)...g) defined in the text (the values of M_{max} are in pN m). $\Delta U = \frac{M_{\text{max}}^2}{2C}$ is the computed expected value

B , the pdfs are Gaussian and the JE is satisfied as indicated in Table 1. Moreover, this happens independently of M_{max} and of the critical value of the ratio $\tau/\tau_{\text{relax}} \ll 1$. Finally, we indicated in Table 1 the value ΔF_{\odot} which is the free energy computed from the JE if one considers the “loop process” from A to A (the same can be done from B to B and the results are quantitatively the same). In principle this value should be zero, but in fact it is not since we have about 5% error in the calibration of the torque M .

4 Conclusion

Our results clearly demonstrate the validity and the robustness of the JE in an isothermal process, at least when the work fluctuations are Gaussian and when the harmonic approximation is relevant for the system. The more accurate and reliable ΔF estimator is given by the crossing points ΔF_{\times} and W_{\times}^{cl} , because they are less sensitive to extreme fluctuations which may perturb the convergence of the JE. We have also shown that, in the case of Gaussian fluctuations, W_{\times}^{cl} remains an excellent estimator even in cases where the JE and the CR could not hold. Unfortunately our results do not fully throw light on the debate between Cohen, Mauzerall and Jarzynski [12, 17] since the work pdfs are Gaussian. Recently, Ritort and coworkers have used the JE to estimate ΔF in an experiment of RNA stretching where the oscillator’s coupling is non-linear and the work fluctuations are non-Gaussian [18]. It would be interesting to check these results on a more simple and controlled system. We are currently working on the experimental realization of such a non-linear coupling, for which $\Delta F \neq -\Delta F_0$. Finally we want to stress that our results, although limited to the Gaussian case, show that it is possible to measure tiny fluctuations of work in a macroscopic systems. As consequence they open a lot of perspective to use the JE, the CR and the recent theorems on dissipated work (see for example [19]) to characterize the slow relaxation towards equilibrium in more complex systems, for example aging materials such as glasses or gels [20].

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